CHAPTER 1

INTRODUCTION

1.1 Introduction

Nowadays, the magnitude to which pollution has reached not only threatens the health and well-being of the population in a particular city, but also produces effects on a global scale. Vehicular emissions have been said to be the main contributor to the air pollution. With the accelerated urbanization and swelling population, the rapid increase in the number of motor vehicles has resulted in the rise of use of petrol. Until today, more petrol stations are still urgently needed to provide more fuel to meet the demand.

The government of Malaysia allows petroleum companies to build more petrol stations due to the increase in the number of automobiles. However, petrol station has been known to be one of the main sources of volatile organic compounds (VOCs) emissions [1]. These compounds include some hazardous air pollutants that would have serious implications on human health and atmospheric environment upon long term exposure. The emission of VOCs into the atmosphere occurs either from the car exhaust or by evaporative emission of fuel (e.g. spillage, tank leakage, refueling process) [2]. It is reported that exposure levels associated with petrol vapor emissions (such as workers in car repair shop, petroleum refineries, dispatch tank trucks, and petrol service stations)

are higher than those associated with motor vehicle emissions (such as bus/commuters, roadside pedestrians, cyclists and car drivers) [1].

Since the implementation of self-service in every petrol filling stations, the VOCs emissions due to evaporative losses while refueling are now directly exposed to consumers who have to be at the vicinity of the filling pumps. Thus, in this study, two adsorbent materials, namely, activated carbon and peat will be investigated on their performance in reducing the VOCs emissions. Optimization on the adsorbing properties will also be studied.

1.2 Petrol Fuel

Petrol fuels are colourless, pale brown or pink blends of volatile liquid-petroleum fractions which can be produced by fractional distillation from crude oil (petroleum oil), catalytic and thermal cracking, hydocracking, catalytic reforming, alkylation and polymerization [3, 4]. These petrol fuels are mixtures of hydrocarbons from $C_5 - C_{12}$ with the approximate boiling range of 30°C to 200°C [5]. Petrol fuels are light and evaporate quickly. The odour can be easily recognized at 0.25 parts of petrol per million parts of air (ppm) [6]. Petrol fuels are ideal for use in spark ignition engines for automotive vehicles [7].

The quality of petrol fuel is indicated by the anti-knocking rating, better known as Octane Number. The octane number of fuel is the percentage by volume of iso-octane in an iso-octane /*n*-heptane mixture with the same knocking tendency as the fuel [8]. *n*-Heptane is assigned an octane number of 0 as it detonated readily at low compression ratios and iso-octane which is highly resistant to detonation is assigned an octane number of 100 [5]. The higher the octane number, the less tendency of a fuel to knock in the spark ignition engines. Higher octane number can be achieved by

increasing the concentration of highly branched iso-paraffin, olefin, and aromatic hydrocarbons in the formulation [7].

1.2.1 Leaded Petrol

In the early 1920's, it was discovered that the antiknock of gasoline could be improved by adding lead anti-knock compounds, particularly tetraethyl lead (TEL) or tetramethyl lead (TML) [4]. An increase in petrol lead content results in an increased octane response. The addition of small quantities of TEL or TML to gasoline greatly causes the petrol fuels to burn evenly and completely [8].

Formulation, in term of increasing the percentage of cyclic hydrocarbons or long-chain materials can also increase the octane-rating. However, it is cheaper to produce petrol with high octane rating by using lead additives [8]. Leaded petrol is produced for use in engines not equipped with catalytic converters. However, when leaded petrol is burned, extremely small particles of lead are emitted into the atmosphere, where they can remain and be inhaled for extended periods of time. These lead particles will enter the body and eventually affect human health especially on children [9]. These serious adverse health effects caused by leaded petrol have resulted in significant changes in fuel compositions.

1.2.2 Unleaded Petrol

Because of the environmental and health concern associated with the lead emissions from vehicles, the world greatly minimize the lead in fuel composition. Many nations are committed to eliminate the use of leaded petrol. The world-wide phasing-out

of leaded petrol has led to the introduction of unleaded petrol in Malaysia on 27 July1990 [10].

The phasing-out of anti-knock lead compounds in petrol fuel has reduced the lead emissions but resulted in a decrease of octane number. However, this can be overcome by using higher octane components (reformate, isomerate, alkylate) or oxygenated components in petrol reformulation to achieve certain octane level. Oxygenated components such as ethers (C_x-O-C_y) and alcohols (C_x- OH) have been used as extender and to compensate for the loss of lead compounds [11].

Most ethers used in petrol are either methyl-tertiary-butyl-ether (MTBE) or ethyl tertiary butyl ether (ETBE). MTBE has almost completely replaced tetraethyllead (TEL) as an octane-booster and is now widely used in the production of unleaded petrol. According to Leong *et al.*, the Royal Thai government issued regulations to phase out the leaded petrol in 1996 by using MTBE as octane enhancer in unleaded petrol [12]. However the use of MTBE contributes towards an increase in 1, 3-butadiene emission which may pose a public health threat [9,12]. Besides ethers, alcohols such as methanol and ethanol are commonly used to reduce anti-knock in unleaded petrol. The use of ethanol as oxygenate in petrol reformulation can also help in the reduction of the emission of VOCs, toxics and nitrogen oxides [12].

In general, unleaded petrol contains a greater proportion of those fuel components that are believed to emit significant quantities of VOCs into atmosphere. The use of unleaded petrol by vehicles not equipped with catalytic converters will also result in an increase in VOC emissions [9]. Therefore, 70% of new vehicles designed today are fitted with catalytic converters which are compatible for use with unleaded petrol. However, it has been found that the use of leaded petrol in catalyst-equipped cars can result in the deposition of lead or lead oxide on cylinder walls, valves and spark plugs. Catalytic converters are also susceptible to poisoning by lead compound in leaded petrol. This has made the introduction of unleaded petrol in the market more necessary [11].

As a result of growing concern regarding the urban atmospheric lead levels, all nations worldwide have been urged to be committed in their support for the use of unleaded petrol on health grounds alone, rather than from the desire to introduce catalytic converters which are poisoned by the lead additives.

1.3 Fuel Additives

There are a large number of additives that can improve the quality of the fuel before it reaches the combustion chamber of an engine. These additives may be added to prevent the gasoline from deteriorating upon storage or during distribution and that deposit formation and corrosion do not occur in the fuel system of an engine. Besides oxygenated compounds that are used as antiknock additives, there are other additives being used in unleaded petrol to improve the performance and stability of gasoline.

1.3.1 Dyes and Markers

The most common reason for using dyes is to meet the legal requirements. In USA, all types of gasoline must be coloured for the purpose of distinguishing one product or brand from another. The dyes are usually red, orange, blue or green and are mainly azo compounds. Treat levels are very low, normally in the range of 2-10 ppm, and it is important that petrol fuels containing dyes do not stain the sides of the light-coloured vehicles if there is a spill during refueling process.

Markers chemical are particularly important for security purposes since they impart no colour to the fuel but are detected either by a colour reaction with another chemical or by other means. Such markers must be detectable without interference by lead alkyls, dyes, and other gasoline additives. Furfural and diphenylamine are often

used as markers and are detected by mixing the gasoline with another chemical to give a colour [11].

1.3.2 Corrosion Inhibitors

The widespread use of alcohols as gasoline octane boosters has increased the corrosivity of gasoline. Internal corrosion of pipelines can reduce flow rates and can give rise to suspended rust in gasoline. To minimize this problem, corrosion inhibitors are added into petrol fuels. Additives are used at comparatively low treat rates, typically, below 20 ppm. The additives used are surfactant materials that attach themselves as a monomolecular layer to the internal surface of the pipeline, thereby protecting it from attack. Many different chemical types are used but all have a polar or hydrophilic group at one end of the molecule and a hydrophobic group such as a long chain alky group at the other. The polar group attaches itself to the metal surface and the non-polar tail sticks into the hydrocarbon phase and provides an oily layer that repels water [11].

1.3.3 Biocides

When microbial activity commences in a petrol tank, the colour and clarity of the petrol and the tank water bottoms change. The colour becomes somewhat darker and suspended matter develops at the fuel/water interface which can block filters, fuel lines and others. Thus, biocides are needed to prevent microbial growth in petrol fuel storage. These additives have a wide range of chemical compositions which may be made up of boron compounds, imines, amines, imidazolines, etc.[11].

1.3.4 Anti-static Additives

When fuels of low electrical conductivity are pumped through pipes, particularly at high velocities, a charge of static electricity can build up in the fuel. This can give rise to sparking as it discharges, and if this happens within a flammable mixture of hydrocarbon vapour and air, a fire or explosion can take place. This problem of static electricity is minimized by adding the anti-static-additive which is mainly a chromium–based organometallic material [11].

1.3.5 Drag-reducing Agents (DRAs)

When the capacity of the pipelines is reduced one possibility to increase the throughput is to add drag-reducing additives in the products going through the pipeline. These additives are extremely high molecular weight polymers which shear very readily and reduce drag by smoothing turbulent burst off the walls of the pipeline and so allow more products to flow. They have been used at concentrations of up to about 50 ppm [11].

1.3.6 Demulsifier and Dehazers

Water can find its way into fuel during refinery processing and distribution and can be present both as free and as dissolved water. Dissolved water can be forced out of solution by a sudden drop in temperature and will appear as a haze that can often take a long time to clear if the petrol is simply left to stand on its own. Besides, when free water is present in the tank, it can sometimes blend with petrol during pumping, and shearing forces involved can give rise to quite stable emulsions that, in severe cases, gives the petrol a milky appearance which can plug filters.

Special anti-haze additives are used in the range of 1-30 ppm in petrol formulation as it effectively prevents haze and emulsion formation. By adding these additives, it would be unusual for these water-sensitivity problems to commence after fuel has reached the vehicle's tank [11].

1.3.7 Odorants

Some petrol blend components have an extremely unpleasant odour due to the presence of certain compounds such as mercaptans. The odour problem can be overcome by refining process such as hydrogen treatment, or the use of low concentrations of compounds such as vanillin (4-hydroxy-3-methoxy-benzaldeyde).

1.4 Volatile Organic Compounds (VOCs)

The volatile organic compounds (VOCs) in the atmosphere comprise many different species with various properties. They constitute a broad range of odorous and toxic substances that include hydrocarbons, olefins, aromatics, and various oxygen-, nitrogen-, sulfur-, and halogen-containing molecules. VOCs are usually organic liquids or solids whose vapor pressure are greater than about 70 Pa and whose atmospheric boiling points are up to about 260°C. They are readily vaporizable at relatively low temperature [13].

Tables 1.1: Classes of volatile organic compounds

Hydrocarbons	Examples	Compounds	Examples
Paraffins	Propane, butane, octane	Alcohols	Methanol, ethanol
Olefins	Ethylene, butadiene	Aldehydes	Formaldehyde
Acetylenes	Acetylene	Ketones	Methyl ethylketone
Aromatics	Toluene, benzopyrene	Acids	Formic acid
		Hydroperoxide	Peroxyacrylnitrite
		Halides	Vinyl chloride
		S compounds	Dimethyl sulfide
		N compounds	Trimethyl amine

VOCs are emitted from various sources such as traffic, natural gas leakage, fossil fuel combustion, petroleum refining and industries (solvent, manufacturing). VOCs that are emitted by motor vehicles such as 1, 3-butadiene, benzene, xylene, toluene, polycyclic aromatic hydrocarbons (PAH) have been identified as hazardous air pollutants (i.e. toxic, mutagenic or carcinogenic) [2]. They are the most serious contributors to atmospheric pollution as they are recognized as important contributors to photochemical smog, acid precipitation and global warming. However, long-term inhalation exposure to those VOCs at certain level may cause diseases such as lung cancer, leukemia and other health effects [2, 9,12]. Thus, control of volatile organic compound emissions is important because they are principal components in the chemical and physical atmospheric reactions that resulted in pollution.

1.4.1 Benzene

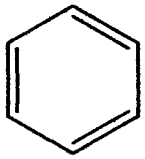


Figure 1.1: Molecular structure of benzene

Benzene, C_6H_{12}, is a hydrocarbon consisting of six atoms each of carbon and hydrogen arranged in a ring structure. It has a molecular weight of 78.1 and boiling point of 80.1 °C. At normal ambient temperature it is a liquid, but it evaporates rapidly at room temperature and is highly flammable. It has a characteristic aromatic odour and is slightly soluble in water (1.5 grams/litre at 20 °C) but miscible with other organic solvents [14].

Benzene is one of the components of petrol. It can escape into the air, particularly from vehicle fuel systems and from filling stations. It is also formed in the motor engine combustion process and emitted in the exhaust. Although in newer cars with catalytic converters, much of the benzene is removed from the exhaust gases, vehicles exhaust still remains the major source of benzene in the air. It is known that benzene is a well-established human carcinogen [9, 14, 15]. After long exposure at certain level of benzene, it may lead to anemia (reduced red blood cells), leucopenia (reduced white cells) and thrombocytopenia (reduced blood platelets) and other health effects [14, 15].

1.4.2 Toluene

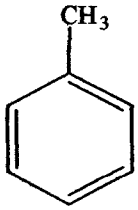
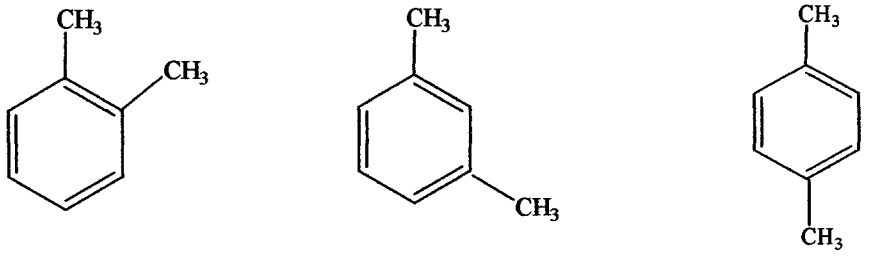


Figure 1.2: Molecular structure of toluene

Toluene is a clear, colourless liquid with an aromatic odour milder than benzene. Other names for toluene include methyl benzene and phenylmethane. Toluene is an alkylbenzene, consisting of a benzene ring and a methyl group and has a molecular formula of C_7H_8. It has a boiling point of 110.6 °C, a vapour pressure of 3.8 kPa at 25 °C, and with a density of 0.8869 g/mL at 20 °C. It is slightly soluble in fresh water (535 mg/L) at 25 °C [15].

Most of the toluene produced is used in the manufacture of benzene. It is commonly used as a solvent or thinner in paints, lacquers, adhesives and petrol additives in achieving selected octane-ratings. The largest source of toluene emissions to air is via the use of toluene as an octane booster in petrol [16]. The presence of toluene in the atmosphere is potentially harmful to human health [12]. Exposure to toluene may result in central nervous system dysfunction. Low to moderate levels can cause tiredness, confusion, weakness, drunken-type actions, memory loss, nausea, loss of appetite, and hearing and colour vision loss. These symptoms usually disappear when exposure is stopped. Inhaling high levels of toluene in a short time can cause light-headed, dizzy, or sleepy. It can also cause central nervous system (CNS) dysfunction and even death [15,16].

1.4.3 Xylene



Ortho- Meta- Para-

Figure 1.3: Molecular structures of xylene isomers

Xylene, $C_6H_4(CH_3)_2$, exists in ambient air as a mixture of ortho-, meta- and para-isomers. It is a clear, colourless liquid with molecular weight of 106.17. The boiling points for each isomer are shown in Table 1.2.

Table 1.2: Boiling points for xylene isomers.

Isomer	Boling point (°C)
Ortho-	144
Meta-	139
Para-	138

It burns readily. Xylene is obtained from crude petroleum and is used widely in many products such as paints, glues, and pesticides. It is found in small amounts in gasoline. The sources of xylene emissions usually come from motor vehicles, aircraft, petroleum refineries and terminals, service stations, lawn mowers and other petrol-fuelled machineries.

Short-term exposure of people by inhalation to high levels of xylene can cause irritation of the nose and throat; gastrointestinal effects such as nausea, vomiting and gastric irritation; mild transient eye irritation and neurological effects. Long-term

inhalation exposure to mixed xylene results primarily in central nervous system (CNS) effects such as headaches, lack of muscle coordination, dizziness, confusion, and changes in one's sense of balance [15].

1.5 Adsorption

Adsorption refers to the trapping of molecules on a high-surface area material. The process is typically used to remove contaminants in fairly low concentrations from a gas stream. The pollutants are adsorbed onto the surface or interstitial areas of adsorbents [13].

There are two types of adsorption. The first is the physical adsorption, where the adsorbed material is held physically, rather loosely by weak physical attraction forces of a dipole or van der Waals nature, and can be released (desorbed) rather easily by either heat or vacuum. Almost all adsorption processes pertinent to air pollution control involve physical adsorption.

The second type is chemical adsorption (or chemisorption), in which chemical bonding forces are also present. The absorbent reacts chemically with the substance being absorbed, and thus holds the absorbed substance much more strongly, requiring more energy to release the absorbed substances [17].

There are several adsorbents used in reducing and controlling VOCs emissions. The surface characteristic and the porosity of the absorbent are important to adsorption process as the properties of VOCs can differ in molecules sizes and polarities [18]. Carbon, zeolite and polymers adsorbents have each been used to adsorb VOCs and other pollutants from relatively dilute concentrations in air to control emissions [19].

Activated carbons are widely used and rather cheap. They are extremely versatile adsorbents of industrial significance and are used in a wide range of applications which are concerned principally with removal of undesired species by adsorption from liquid or gases, in order to effect purification or the recovery of chemical constituents [20]. Another adsorbent is zeolite which has the alumino-silicate crystal structure and uniform pore size. The pores on the surface allow the VOC molecules to be adsorbed on the interior area of the zeolites. They are thermally and chemically stable products and are easily regenerated without loss of performance [21]. However, polymeric adsorbents have built-in pores when they are manufactured. These pores can range from macroporous through molecular sizes, but the smallest pores are usually larger than micropores of the carbon. These adsorbents can desorb faster than carbon [19]. Besides, peat which possesses good physical and chemical properties has also been used as absorbent in reducing the organic contaminants in waste waters [22].

1.5.1 Activated Carbon

Activated carbon which is characterized by their highly developed internal surface and porosity, and strong adsorption capacity has long been recognized as one of the most versatile adsorbents to be used for effective removal of organic contaminants in liquids or gases [23].

The adsorption capacity of activated carbon depends strongly on its surface microstructure [18]. The pores in activated carbons are scattered over a wide range of size and shape. The pores are usually classified by their sizes and divided into three groups: (i) micropores having average diameter more than 50 nm, (ii) mesopores with diameter 2-50 nm, and (iii) micropores having average diameter less than 2 nm. These are further divided into supermicropores (0.7-0.2 nm) and ultramicropores of diameter less than 0.7 nm [20]. Figure 1.4 depicts the adsorption process showing transfer of adsorbate molecules through the bulk gas phase to the surface of the solid and diffuse

onto the internal surfaces of the pores in the solid adsorbent. Thus the adsorption capacity of activated carbon depends strongly on the type of pore and the total surface area available for adsorption.

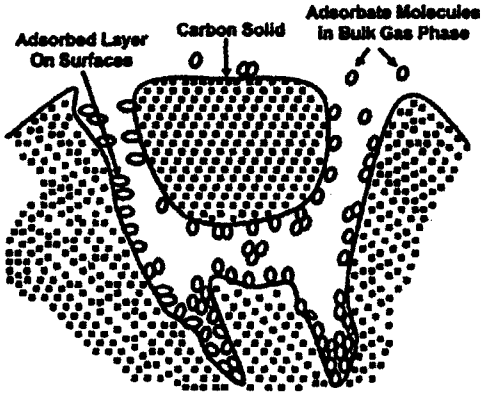


Figure 1.4: Adsorption process in activated carbon: Transfer of adsorbate molecules to adsorbent [20].

Activated carbons are effective in the removal of odour, colour, taste and other undesirable organic impurities from potable water in the treatment of domestic and industrial waste water. They are also used in air purification in places such as restaurants, food processing and chemical industry, in air pollution control, in purification of many chemicals, pharmaceutical and food products and in a variety of gas phase applications. Besides, they are also used as catalyst and catalyst support along with other inorganics [20].

Activated carbons can be made from a variety of low cost raw materials such as peat, coal, nut shell, lignite, saw dust and synthetic polymers. Due to their low cost and unique properties, this makes activated carbon a more versatile adsorbing material and a promising method in reducing VOCs.

1.5.2 Peat

Peat is a naturally occurring substance that formed from the remains of the incomplete decomposition of plant and animal life associated with wetlands. The organic materials partially decay into peat, called the humification process, which is brought about partly by micro-organisms. It forms in situation where the rate of the production of organic material exceeds the rate of decomposition. Peat is brownish-black in colour and in its natural state is composed of 90% water and 10% solid material [22].

Peat is composed primarily of the carbon rich incompletely decomposed remains of plants and animals and is biologically stable under appropriate conditions. Peat has typically low conductivity and pH of the peat is highly correlated to the decomposition rate. The greater the decomposition rate, the higher the pH [23]. It is generally odour free and does not contain toxic xenobiotic substances such as heavy metals. The chemical composition of peat depends on the formation process, the quality of the bedding, groundwater flow, amount of precipitation, and even, to some degree, the impact of airborne particles. Decomposition of peat such as the degree of humification, also plays a role and determines the peat's chemical composition. Low-humified peat contains the most cellulose, while high-humified peat contains various humus substances.

Research in the United States has shown that peat is effective in removing phenol, odorous gases, textile dyes, alkyl benzene sulphonate (ABS) found in detergents, and heavy metals from a variety of municipal and industrial wastes. The first use of peat for domestic waste water treatment was documented by Brooks (1980) [24]. According to Asplund *et al.* (1976), peat has a large specific area (< 200 m^2/g) and is highly porous (95%). It has excellent ion exchange properties which is being similar to natural zeolites. Due to its high ion exchange capacity and its polar characteristic, peat is capable of removing pollutants from waste water [25] and is a good absorbent material. However, its performance on the organic pollutants is not widely discussed.

1.6 Problem Statement

Vehicular emission is the major contributor to poor air quality. The emissions of VOCs are strongly dependant on the composition of the fuels used. There is growing evidence that unleaded fuels resulted in an increase in VOCs emissions [9]. Since VOCs emission is mainly associated with the composition of the fuels, the pollution prevailing in the vicinity of petrol stations has become the main concern.

Emissions from petrol stations are associated with two main sources [2]:

- Displacement of the headspace vapour from the underground storage tanks when road tankers are refilling the tanks. The mass emission rate will be relatively high, but only during the short periods of refilling.
- Displacement of the headspace vapour from the tank of the car as it is refuelled.

VOCs which are released such as benzene, MTBE, toluene, 1,3-butadiene and aromatic hydrocarbon are hazardous to the atmospheric environment. The emissions of VOCs are the precursor for the formation of photochemical smog and tropospheric ozone, and the depletion of the stratospheric ozone layer [26]. On a more serious note, long term exposure to VOCs such as benzene and 1,3-butadiene can cause a variety of adverse health effect on human such as leukaemia, lung cancer, asthma and other diseases [9].

Therefore, several researches aiming at reducing the VOCs emission have been carried out.

1.7 Importance of Research

The emissions of VOCs into atmosphere not only affect the natural environment, but pose a great impact on human health. Along with the rapid growth of the number of motor vehicles, increases of VOCs emissions definitely will lead to the severity of air pollution. Therefore, reduction of these compounds will be the subject of intense study in this research.

Adsorption technique is used to reduce the emissions of VOCs as it is the most effective and most economical method [26]. Activated carbon and peat will be used in this study as adsorbents for VOCs which are released during petrol filling process. The adsorbed VOCs will then be desorbed before they are analyzed by gas chromatography.

These adsorbents will be studied and comparison between activated carbon and peat in reducing the emissions of VOCs will be investigated. Hopefully, the emission of VOCs into atmosphere can be reduced by using the most effective adsorbent materials.

1.8 Research Objective

The purpose of this research is to study the effectiveness of the activated carbon adsorbent and peat as adsorbents in reducing the VOC emission during the refueling process in petrol station.

Objectives of this research are:

(i) To investigate the adsorbent performance of activated carbon on petrol vapour.

(ii) To investigate the use of the peat as adsorbent for petrol vapour.

(iii) To compare the effectiveness of both adsorbents in reducing the emission of VOCs to the atmosphere during refueling process at vicinity of petrol station

(iv) To design, fabricate and install a device which will reduce VOC emissions during petrol filling process.

1.9 Scope of Research

This research is designed to study the effectiveness of selected adsorbent materials in reducing VOCs emission. Activated carbon and peat are the two adsorbents that will be studied in this research. The five selected VOCs that will be analyzed are benzene, toluene, *p*-xylene, *m*-xylene and *o*-xylene. They are chosen because of their known occurrence in the vicinity of petrol station and the proven toxicity and health hazardous.

The sampling of selected VOCs will be carried out in laboratory. The scope of research is as follows:

- Identify the target VOCs and determine their concentrations that evaporate from the petrol in laboratory by using gas chromatography.
- Compare the concentration of VOCs released in different setting, namely, with adsorbent and without adsorbent.
- Optimize the parameters for adsorbents
- Determine and compare the effectiveness of the adsorbents in VOCs reduction.